THE PROPERTIES OF SOME LICHEN AND FUNGUS PIGMENTS

BY

JAMES NEWTON COKER

B.S., Birmingham-Southern College, 1943
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE COLLEGE OF
THE UNIVERSITY OF ILLINOIS, 1950

URBANA, ILLINOIS
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THE PROPERTIES OF SOME LICHEN AND FUNGUS PIGMENTS

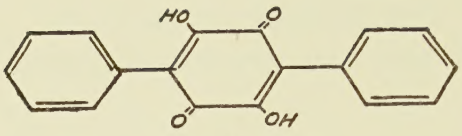
Introduction

Several substituted terphenyl derivatives have been shown by Kögl to occur naturally as fungus pigments. One of these materials, polyporic acid, is the coloring matter in the fungus *Polyporus nidulans* and is present in amounts as high as 43 per cent of the dry weight of the fruit body. Both degradation studies (1) and a synthesis of the material by Adams and Shildneck (2) have shown that polyporic acid is 2,5-dihydroxy-1,4-diphenylbenzoquinone (I). The purpose of the work reported here was to investigate some of the more interesting properties of this pigment, relating these properties wherever possible to compounds of related structure. It was further desired to devise a method of converting polyporic acid to the lichen pigment, vulpinic acid (II). Finally it was hoped that the structures of rhizocarpic acid (III) and epanorin (IV), two pigments which have been isolated from the lichen *Lecanora epanora* and known to be pulvinic acid derivatives, could be elucidated and that methods of synthesis could be devised for these compounds.

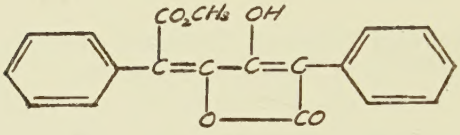
All of these objectives were successfully realized.

Discussion of Results

The synthesis of polyporic acid (I) was accomplished by a modification of the method of Adams and Shildneck (2). 1,4-Benzoquinone was treated with excess benzene in the presence of anhydrous aluminum chloride to yield a mixture of quinones, quinhydrones and hydroquinones. Nitrous acid was found to be a better oxidizing agent than chromic acid, the oxidant suggested in the previous work, for converting the diphenylated materials present in this mixture to 2,5-diphenyl-1,4-benzoquinone (3). By the direct bromination of 2,5-diphenyl-1,4-benzoquinone, 2,5-dibromo-1,4-diphenylbenzoquinone was obtained in 92 per cent yield. Hydrolysis of the dibromoquinone with aqueous alcoholic sodium hydroxide yielded polyporic acid quantitatively.



I



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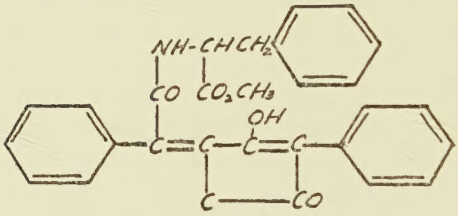
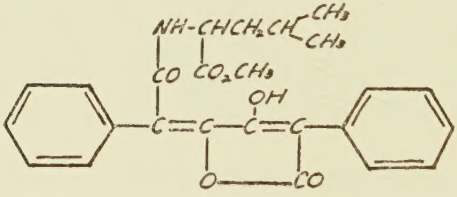


III



IV

Lead tetraacetate in boiling glacial acetic acid reacts smoothly with polyporic acid to give pulvinic acid lactone in a yield of 37 per cent. The lactone can be easily converted into vulpinic acid (II) by heating with methanolic hydrochloric acid. The synthetic vulpinic acid was observed to correspond exactly in its physical properties and reactions with the natural product (4).

Spiegel has described the formation of a by-product in the pyrolysis of vulpinic acid to pulvinic acid lactone. His analysis of the compound would indicate that it is isomeric with vulpinic acid and on this basis named it "isovulpinic acid." This compound has been prepared and was found not to be an isomer of vulpinic acid. It is instead identical with ethyl pulvinate.

Rhizocarpic acid (III) and epanorin (IV), the only two lichen pigment which have been reported as containing nitrogen, are pulvinic acid derivatives, as indicated by alkaline degration studies (5, 6, 7). Both pigments occur in a number of lichens.

The correct analysis of rhizocarpic acid was determined to be $C_{28}H_{23}O_6N$ by Jones, Keane and Nolan (5) in 1944. In the present investigation rhizocarpic acid has been found to be the methyl ester of L-N-pulvinyl-β-phenylalanine (III). The synthetic product, prepared by the reaction of pulvinic acid lactone with the methyl ester of L-β-phenylalanine, did not depress the melting point of a sample of the natural product and its infrared absorption spectrum was identical with that given by the natural pigment. Synthetic rhizocarpic acid yielded two derivatives, L-N-pulvinyl-β-phenylalanine and L-N-pulvinyl-β-phenylalanine, ethyl ester, which melted correctly for similar derivatives reported for the natural product.

Epanorin, $C_{25}H_{25}O_6N$, corresponds in its chemistry to rhizocarpic acid (5) and has been shown by a similar synthesis to be the methyl ester of L-N-pulvinylleucine (IV).

An interest in the properties of polyporic acid (I) has prompted a study of the metallic complexes of 2,5-dihydroxy-1,4-benzoquinones. Most of the work has been carried out with the readily available parent compound, 2,5-dihydroxy-1,4-benzoquinone. Both compounds were observed to form a large number of highly insoluble complexes. Because these materials were almost without exception highly hydrated, their analyses were best interpreted by a consideration of carbon-to-metal ratios. Complexes in which the quinone-to-metal ratio was 2:1, 1:1 and 1:2 were obtained.

The ability of polyporic acid to form insoluble complexes with most metallic ions may be of some importance in connection with its occurrence in nature. The free acid may function to protect the spores against microörganisms and insects by precipitating and thereby removing essential minerals from these invaders. Samples of *Polyporus nidulans* were found to have an abnormally low ash content. Analysis of the ash present has shown that it is composed largely of potassium and sodium salts, cations which are incapable of complexing with the quinone. This would indicate that polyporic acid is present in the fruit body almost entirely in the uncomplexed form, and conforms with the idea that the compound functions in the defense mechanism of the plant.

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VITA

The author was born in Birmingham, Alabama, on May 4, 1922. He graduated from high school in 1939 and in 1943 received the degree of Bachelor of Science from Birmingham-Southern College. He served in the United States Army Air Corps from March, 1943, to December, 1945. In March, 1946, he entered the Graduate College of the University of Illinois and received the degree of Master of Science in June, 1947. From February, 1947, until February, 1950, he held a part-time assistantship in organic chemistry.

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